

(51)Int.Cl. ⁷	識別記号	特開平11-39747	(71)出願人	000005108	株式会社日立製作所
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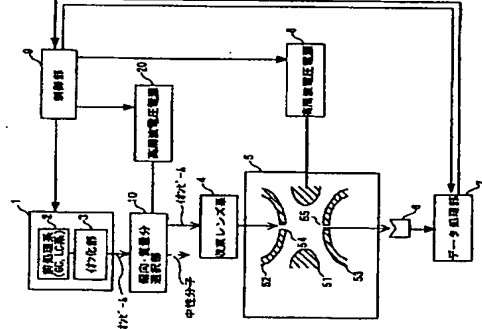
(54) 【発明の名称】 イオントラップ型質量分析装置およびイオントラップ質量分析方法

(57) 【要約】

【課題】 質量分析すべき試料イオンの濃度を高めて、高分解能に、かつ、より高いS/N比で、質量分析を行うことができるイオントラップ型質量分析装置およびイオントラップ質量分析方法を提供する。

【解決手段】 イオントラップ型質量分析部5で質量分析を行う前に、偏向・質量選択部10の偏向四重電極系11で、不要なイオンや中性分子を除去する。偏向四重電極系11は4本の電極15を有し、各電極15は各電極間距離が一定であるように同じ方向に同底面湾曲している。

図 1



前記イオンビームは4つの前記棒電極間を通過することと特徴とする請求項9のイオントラップ質量分析方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、イオン化された溶媒分子と試料をイオントラップ電極間に供給して、高感度でイオンの質量を分析するイオントラップ型質量分析装置およびイオントラップ質量分析方法に関するものである。

【0002】

【従来の技術】 混合物試料を質量分析する場合、混合物試料を成分分離する前処理系と、質量分析系とを結合させることにより、より高精度な分析が可能となる。通常、前処理系としてガスクロマトグラフや液体クロマトグラフなどが用いられる。前処理系はガスクロマトグラフや液体クロマトグラフでは、固定相をつめたカラム中に、ガスクロマトグラフの場合は中性ガス、液体クロマトグラフの場合は溶媒とともに混合物試料を流し、固定相に対する吸着力の違いにより混合物試料を分離していき、ガスクロマトグラフや液体クロマトグラフ等の前処理系で成分分離された試料は、イオントラップ型質量分析系に導入する前にイオン化される。このとき、溶媒分子も同時にイオン化されるが、中にはイオン化されず中性状態のまま存在するものも生じる。中性状態の溶媒分子は検出時のノイズの原因となるため、除去する必要がある。

【0003】 特開平5-325882 号公報や特開平7-85834 号公報は、偏向電極を用いて、溶媒分子と試料が含まれるイオンビームを偏向して質量分析部に供給し、偏向されない中性分子は取り除くことを記載する。

【0004】

【発明が解決しようとする課題】 上記従来技術の偏向電極を用いて中性分子とイオンとを分離することはできるが、イオンの質量選択性はなく、イオン化された溶媒分子は取り除くことはできない。

【0005】 従来のイオントラップ型質量分析装置の場合、イオン化された溶媒分子と試料が一緒にイオントラップ電極間に捕獲されるので、イオントラップ電極間の空間のイオンの密度が大きくなりすぎて、分解能が低下したり、マスシフトが発生したりして分析性能が低下することがある。分析性能を維持して質量分析するためには、イオントラップ電極間に捕獲できるイオンの数に限界があり、1度に多量の試料を質量分析することはできない。特に、前処理系として液体クロマトグラフを用いる場合、イオン化される溶媒分子の数は、試料イオン数の約3〜5桁多くなるため、溶媒イオンがイオントラップ電極間に捕獲されたイオンの多数を占めて、質量分析に必要な量の試料イオンがイオントラップ電極間に供給できなくなる問題が生じる。

【0006】 イオン化された溶媒分子と試料をイオン

【00332】したがって、不要なイオンの q_0 の値が安定透過領域外になるように棒電極14に印加する電圧 $V_0 \cos \omega_0 t$ を調整することにより、不要イオンを除去できる。このように、四重棒電極系13の棒電極14に印加する電圧 $\pm V_0 \cos \omega_0 t$ を調整することにより、イオンの質量対電荷比 m/N に応じて選択的に棒電極間を透過させることができる。

【00333】本実施例でも、図4に示す棒電極12に印加する電圧 $\pm V_0 \cos \omega_0 t$ を調整して、上述したのと同様なイオンの質量選択を行うことができる。また、偏向四重棒電極系11の棒電極12に印加する電圧 $\pm V_0 \cos \omega_0 t$ は、液曲した棒電極12に沿って液曲している。選択されたイオンは液曲した四重棒電極系11から出射されるが、中性分子は入射した方向へ直進するから、選択されたイオンと分離される。したがって、中性分子が除去されて、選択されたイオンのみが、イオントラップ型質量分析部5に輸送される。

【00334】図7に、溶媒分子が9.0amu以下で、9.0amu以下の質量数のイオンを不要イオンとした場合の偏向四重棒電極系11でのイオンの軌道解析の例を示す。不要な9.0amuのイオンの (a_0, q_0) を、図8の $(0, 0.908)$ に相当するように、高周波電圧 $\pm V_0 \cos \omega_0 t$ を設定した。

【00335】図7の解析結果によると、9.0amu以下の不要イオンは不安定となり偏向四重棒電極系11から除去されるが、それより高質量数イオンに対しては安定に通過している。また、安定に通過したイオン軌道の中心軸は、液曲した棒電極12の形状に沿って曲っており、安定に通過したイオンはイオントラップ型質量分析部5へ進入できる。しかし、中性分子は四重棒電極系11で直進するから、イオントラップ質量分析部5へ進入できない。

【00336】従って、本実施例のイオントラップ型質量分析装置によれば、偏向四重棒電極系11で不要なイオンや中性分子を除去して、質量分析すべき試料イオンの高質量を高めることができるので、多量の不要なイオンによる低分解能化及び中性分子によるノイズの発生などの悪影響を受けずに、より高分解能に、かつ、より高いS/N比で、質量分析を行うことができる。

【00337】また、本実施例で説明した偏向四重棒電極系11では、イオンビームが偏向四重棒電極系11を通過する前後で、ビーム進行方向がほぼ平行であるので、図9に示すように、イオン源からイオンが入射してくる方向とイオントラップ型質量分析部5のエンドキャップ電極52、53の軸とが一致している既存の装置に對し、軸をずらすだけで容易に対応可能である。

【00338】(実施例2) 次に、本発明の第2の実施例について説明する。本実施例では、偏向・質量選択部1

0の偏向四重棒電極系111において、図10に示すように、イオンビームの入射方向と出射方向が異なるように液曲させた棒電極15を用いた。ただし、棒電極15は電極間距離が変わらないように、かつ、イオンビームの入射方向と出射方向が約90°をなすように棒電極12を液曲させてある。このように棒電極12を液曲させてあると、さまざまな角度をもって偏向四重棒電極系11に入射して来る中性分子に対しては、選択されたイオンと分離することができる。

【00339】本実施例によれば、中性分子をより除去することができ、より高分解能に、かつ、より高いS/N比で、質量分析を行うことができる。

【00340】(実施例3) 本発明の第3の実施例について説明する。本実施例では、図11に示すように、偏向四重棒電極系111の棒電極12に印加する電圧を、高周波電圧 $V_0 \cos \omega_0 t$ ばかりでなく直流電圧 U_0 ($U_0 \neq 0$)も印加する。(2)式により、イオンの (a_0, q_0) 点も、図12の $a_0 = 2U_0 q_0 / V_0$ の直線上に並び、この $a_0 = 2U_0 q_0 / V_0$ の直線と安定透過領域が重なる領域内に相当するイオンのみが安定に四重棒電極系11を通過し、それ以外のイオンは軌道が不安定化して除去される。安定に四重棒電極系11を通過したイオンの質量範囲を M_1 [amu] とすると、イオントラップ型質量分析部5で最終的に得られるマススペクトルは、図13に示されるように、 M_1 [amu] $\sim M_2$ [amu] の範囲内に限られる。

【00341】したがって、質量分析すべきイオンの質量範囲が分かっている場合は、上限値および下限値に対応する (a_0, q_0) が安定領域にあるように、棒電極12に印加する電圧 $\pm (U_0 + V_0 \cos \omega_0 t)$ を調整すればよい。

【00342】また、図14に示すように、 $a_0 = 2U_0 q_0 / V_0$ の直線が安定透過領域の頂点付近を横切るように、 $U_0 + V_0 \cos \omega_0 t$ を調整する。このように棒電極12に電圧を印加すると、図14で安定透過領域の頂点付近に相当する質量対電荷比 M_0 を持つイオンが四重棒電極間を安定通過し、それ以外の全てのイオンは除去される。また、第1の実施例と同様に、偏向四重棒電極系11から中性分子が除去される。したがって質量対電荷比 M_0 を持つイオンのみが、イオントラップ型質量分析部4に入射され、イオントラップ電極間にトラップされて安定振動することになる。

【00343】本実施例によれば、第1の実施例による効果に加え、イオンの選択範囲をより限定できるため、より高分解能に、かつ、より高いS/N比で、質量分析を行うことができる。

【00344】(実施例4) 次に、本発明の第4の実施例であるイオントラップ型質量分析装置について説明する。図15に、本実施例のイオントラップ型質量分析装置の概略図を示す。本実施例のイオントラップ型質量分

3の棒電極14間に入射したイオンは、棒電極14間で質量選択され、その後、偏向電極33で中性分子が除去される。

【0051】本実施例によれば、平行な4本の棒電極14と、偏向電極33および収束レンズ系32を用いることができるため、偏向・質量選択部10を容易に製作できる。

【0052】(実施例7) 次に、本発明の第7の実施例について説明する。本実施例では、偏向・質量選択部10に四重棒電極系13と、偏向八重棒電極系34などの多重棒電極を用いる。本実施例では、質量選択性が優れた四重棒電極系13でイオンビームの質量を選択し、偏向八重棒電極系34で図21に示すように液曲させ、イオンビームを偏向させる。偏向八重棒電極系34はイオン軌道の安定性に優れているため、電極の液曲などにもイオンは追従して安定に偏向する。また、図22に示すように、四重棒電極系13での質量選択と偏向八重棒電極系34でのビーム偏向の順序が逆でもよい。

【0053】本実施例によれば、四重棒電極系13でイオンビームを質量選択し、偏向八重棒電極系34でイオンビームを安定に偏向させることにより、イオンビームの偏向によるイオン損失を少なくして、より高感度の質量分析ができる。

【0054】(実施例8) 次に、本発明の第8の実施例について説明する。本実施例では、図23に示すように、偏向・質量選択部10に、平行な4本の棒電極14から成る四重棒電極系13を複数用いる。各四重棒電極系13は、それぞれの中心軸が交差するように設置されている。イオンビームは、各四重棒電極系13で質量選択され、隣り合う四重棒電極系13との間で偏向される。隣り合う四重棒電極系13との間で中性分子が除去される。

【0055】また、各四重棒電極系13で異なる不要イオンを除去することもでき、より限定した質量対電荷比の範囲のイオンを選択できる。例えば、試料中に、不要なイオンとして、質量対電荷比 M_1 が M_1 以下であるイオン、 M_2 ($M_1 < M_2$) であるイオン、および、 M_3 ($M_1 < M_3$) であるイオンが含まれている場合、四重棒電極系25-aで、 M_1 以下の質量対電荷比のイオンを除去し、四重棒電極系25-bに補助交流電圧を印加して、 $M=M_2$ の質量対電荷比のイオンを除去し、そして、四重棒電極系25-cに補助交流電圧を印加して、 $M=M_3$ の質量対電荷比のイオンを除去すればよい(図24参照)。各四重棒電極系13で異なる不要イオンを除去するためには、各四重棒電極系13で棒電極14に印加する補助交流電圧をそれぞれ調整する。

【0056】本実施例によれば、選択すべき質量範囲が不連続である場合も、不要なイオンと中性分子を除去することができ、より高分解能に、かつ、より高いS/N比で、質量分析を行うことができる。

【0057】

【発明の効果】本発明によれば、イオン化された試料とともに中性分子が偏向・質量分離選択部に供給されても、イオンビームは偏向・質量分離選択部で偏向され、かつ、質量選択された、中性分子は入射した方向へ進むから、選択されたイオンと中性分子とが分離され、イオントラップ型質量分析部で質量分析されるべき試料イオンの濃度を高めることができるので、多量の不要なイオンによる低分解能化及び中性分子によるノイズの発生などの悪影響を受けずに、より高分解能に、かつ、より高いS/N比で、質量分析を行うことができる。

【0058】また、偏向・質量分離選択部が、同じ方向に湾曲している4つの棒電極を有することにより、選択されたイオンと中性分子とを分離することができる。

【0059】また、棒電極には高周波電圧から高周波電圧を印加して、棒電極間に四重極電界を形成する。高周波電圧が直流成分を持たないものである場合は、交流電圧の振および周波数に基づいて求められる質量数対電荷比以下のイオンが棒電極間から除去される。高周波電圧が直流成分と交流成分を有する場合は、直流電圧の大きさと交流電圧の振および周波数とに基づいて求められる質量数対電荷比の範囲のイオンが棒電極間から除去され、高周波電圧が2つの交流成分を有する場合は、質量分析すべきイオンの質量範囲に点在する不要イオンを排除することができる。

【0060】また、偏向電極でイオンビームを偏向して中性粒子を除去でき、4つの平行な棒電極でイオンを選択してもよい。偏向電極に湾曲した八重極電極を用いると、イオンビームの偏向によるイオン損失を少なくでき、より高感度の質量分析ができる。

【0061】また、4つの平行な棒電極の組を複数用いて、各電極間の中心軸が交差するように直列に配置すれば、選択すべき質量範囲が不連続である場合も、不要なイオンと中性粒子を除去することができる。

【符号の説明】

【図1】第1の実施例のイオントラップ型質量分析装置の概略図。

【図2】イオントラップ型質量分析部5を示す図。

【図3】イオントラップ電極間の安定領域を示す図。

【図4】偏向・質量選択部10の偏向四重極電極系11を示す図。

【図5】平行な4本の棒電極14を有する四重極電極系13を示す図。

【図6】四重極電極系13の棒電極14間の安定領域を示す図。

【図7】偏向四重極電極系11におけるイオンの軌道解析の例を示す図。

【図8】偏向四重極電極系11の棒電極12間の安定領域を示す図。

【図9】既存の装置と本実施例との比較図。

【図10】第2の実施例における偏向四重極電極系11の棒電極15を示す図。

【図11】第3の実施例における偏向四重極電極系11の棒電極12を示す図。

【図12】第3の実施例における偏向四重極電極系11の安定領域を示す図。

【図13】第3の実施例において得られるマススペクトルを示す図。

【図14】第3の実施例における偏向四重極電極系11の安定領域を示す図。

【図15】第4の実施例のイオントラップ型質量分析装置の概略図。

【図16】第4の実施例における偏向四重極電極系11の棒電極12を示す図。

【図17】第4の実施例における偏向四重極電極系11の安定領域を示す図。

【図18】第5の実施例における偏向・質量選択部10を示す図。

【図19】第6の実施例における偏向・質量選択部10を示す図。

【図20】第6の実施例における偏向・質量選択部10の他の例を示す図。

【図21】第7の実施例における偏向・質量選択部10を示す図。

【図22】第7の実施例における偏向・質量選択部10の他の例を示す図。

【図23】第8の実施例における偏向・質量選択部10を示す図。

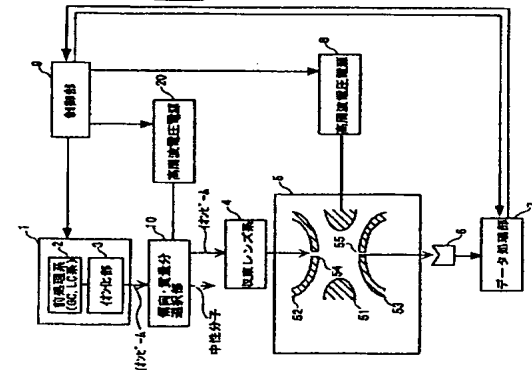
【図24】第8の実施例における四重極電極系11の安定領域を示す図。

【符号の説明】

1…イオン源、2…前処理系、3…イオン化部、4…収束レンズ系、10…偏向・質量選択部、5…イオントラップ型質量分析部、6…検出器、7…データ処理部、8、20…高周波電圧電源、9…制御部、51…リング電極、52、53…エンドキャップ電極、54、55…中心口、11…偏向四重極電極系、13…四重極電極系、12、14、15、16…棒電極、21…補助交流電圧電源、31…減速電極、32…収束レンズ系、33…偏向電極、34…偏向八重極電極系。

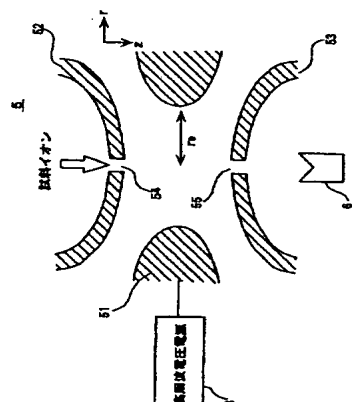
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図1



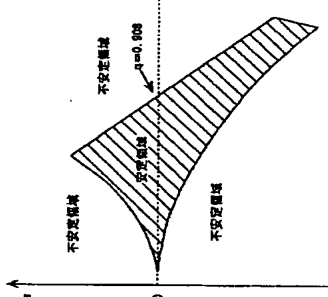
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図2



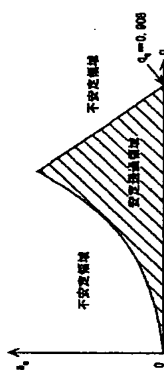
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図3

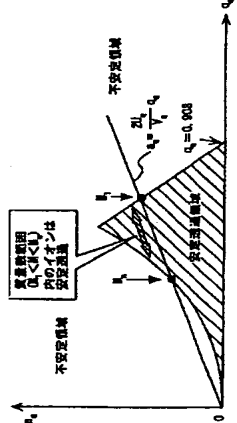


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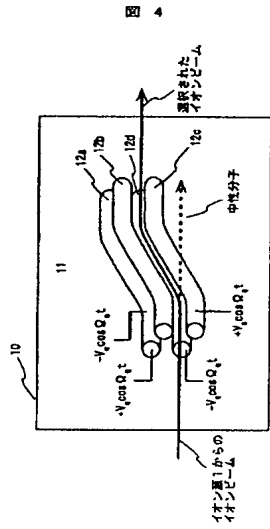
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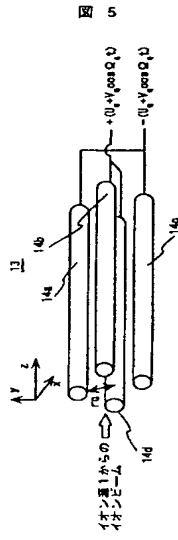
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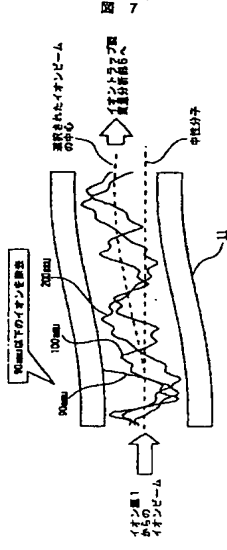
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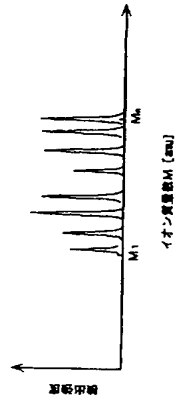
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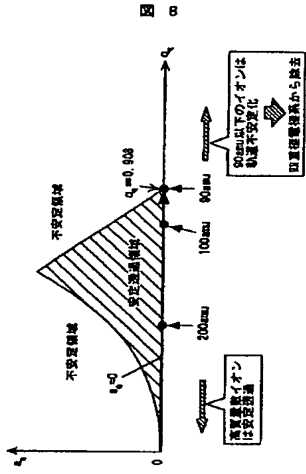
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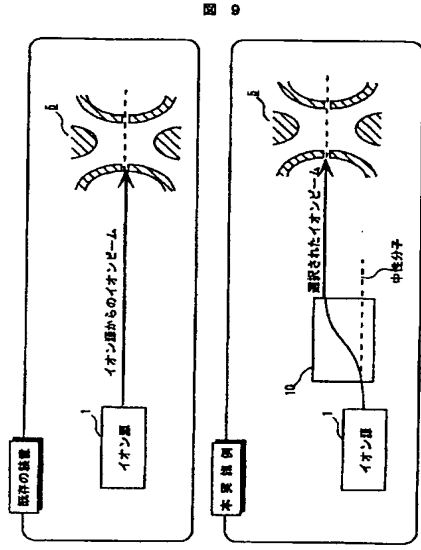
【図13】



【図8】

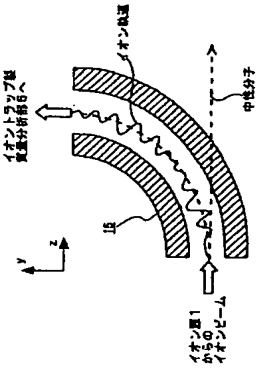


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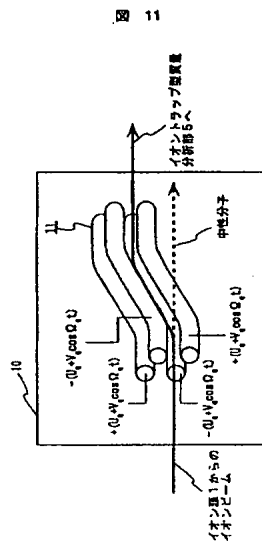


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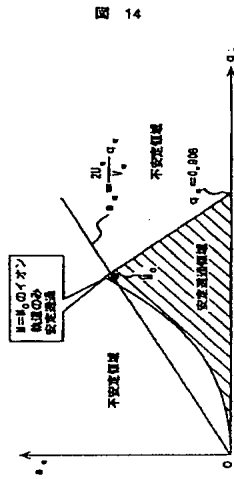
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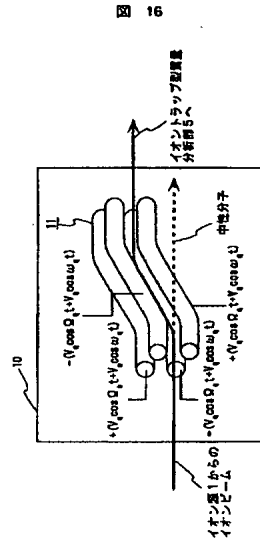
【図11】



【図14】

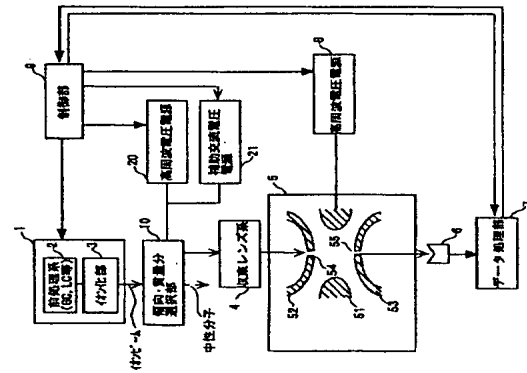


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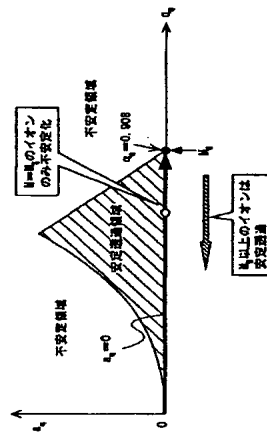


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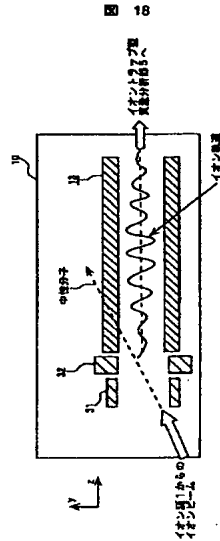
図 15



【図17】

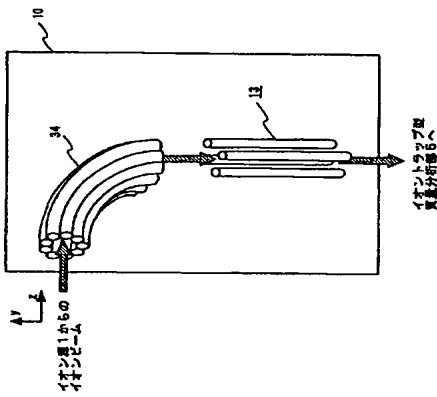


【図18】



【図22】

図 22



【図19】

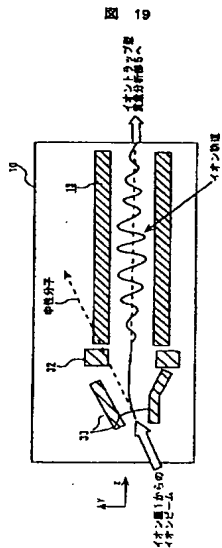


図 19

【図20】

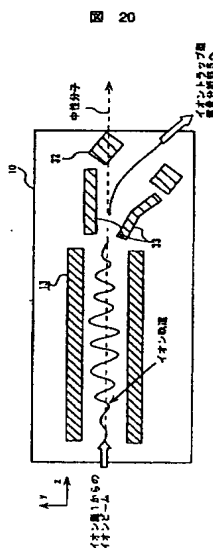


図 20

【図21】

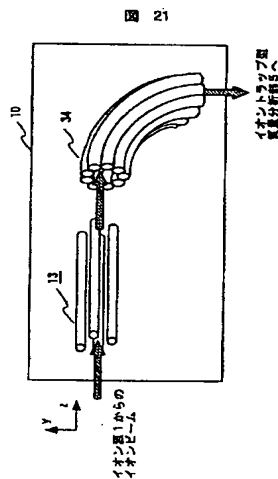


図 21

【図23】

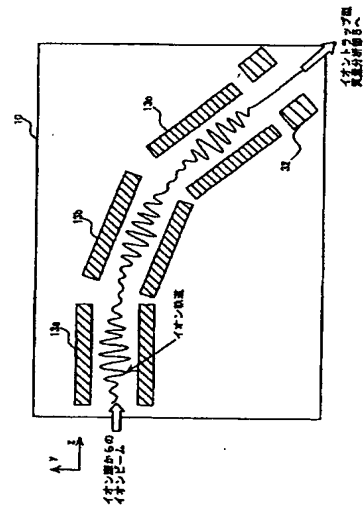


図 23

【図24】

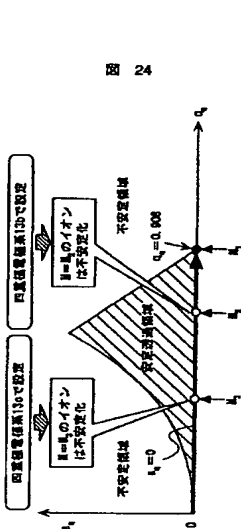


図 24

フロントページの続き

(51) Int. Cl. 7	識別記号	F I	チャート (参考)
G 0 1 N 30/72		G 0 1 N 30/72	C
H 0 1 J 49/06		H 0 1 J 49/06	
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	Fターム(参考) 5C038 PF07 PF10 JJ02 JJ06 JJ09		Fターム(参考) 5C038 PF07 PF10 JJ02 JJ06 JJ09
			JJ11

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-243347

(43)Date of publication of application : 08.09.2000

(51)Int.Cl.

H01J 49/42

G01N 27/62

G01N 30/72

H01J 49/06

(21)Application number : 11-039747

(71)Applicant : HITACHI LTD

(22)Date of filing : 18.02.1999

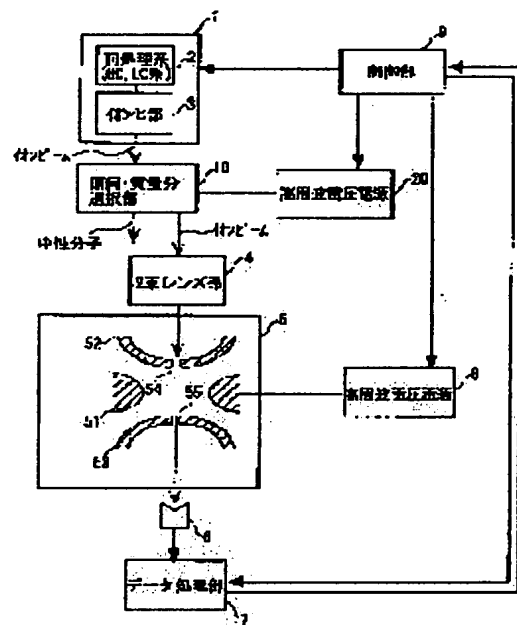
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(54) ION TRAP TYPE MASS SPECTROMETER AND ION TRAP MASS SPECTROMETRY

(57)Abstract:

PROBLEM TO BE SOLVED: To increase ion concentration of a sample and to make mass spectrometry with high resolution and a high S/N ratio by deflecting an ion beam containing the ionized sample, and feeding the ion beam containing ions with the selected mass to an ion trap type mass spectrometric section.

SOLUTION: A mixed sample subject to mass spectrometry is component-separated by a preprocessing system 2, the mixed sample and a solvent are ionized by an ionization section 3, unnecessary ions and neutral molecules are removed by a deflection mass selection section 10, and the mixed sample is fed to an ion trap type mass spectrometric section 5 through a focusing lens system 4. The mass spectrometric section 5 is composed of a ring electrode 51 and end cap electrodes 52, 53 facing each other across the ring electrode 51, and a DC voltage and a high-frequency voltage are applied between the electrodes from a high-frequency voltage power supply 8 to form the quadrupole electric field between the electrodes. An ion beam from the focusing lens system 4 is fed between the ring electrode 51 and the end cap electrodes 52, 53 through a center port 13, is captured by the quadrupole electric field, and is detected by a detector 6 through a center port 55, then a mass spectrum is obtained as the final analysis result.



LEGAL STATUS

[Date of request for examination] 21.02.2003

[Date of sending the examiner's decision of rejection] 09.11.2004

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] In the ion trap mold mass spectroscopy which has the ion trap mold mass analysis section which catches an ion beam by quadrupole electric field, and carries out mass separation of the caught ion The deflection and the mass discontinuous-selection section which deflects the ion beam containing the ionized sample, and chooses the mass of ion The ion trap mold mass spectroscopy characterized by supplying the ion beam containing the ion which prepared for the preceding paragraph of said ion trap mold mass analysis section, and was chosen in said deflection and mass discontinuous-selection section to said ion trap mold mass analysis section.

[Claim 2] Said deflection and mass discontinuous-selection section are the ion trap mold mass spectroscopy of claim 1 which has four pin electrodes and is characterized by said four pin electrodes curving in the same direction.

[Claim 3] The ion trap mold mass spectroscopy of claim 2 characterized by having the RF generator which impresses high-frequency voltage to said pin electrode.

[Claim 4] Said high-frequency voltage is the ion trap mold mass spectroscopy of claim 3 characterized by being the superposition electrical potential difference of high-frequency voltage and direct current voltage.

[Claim 5] Said high-frequency voltage is the ion trap mold mass spectroscopy of claim 3 characterized by being the superposition electrical potential difference of two high-frequency voltage from which a frequency differs.

[Claim 6] Said deflection and mass discontinuous-selection section are the ion trap mold mass spectroscopy of claim 1 characterized by having the deflecting electrode which deflects said ion beam, and four parallel pin electrodes.

[Claim 7] Said deflecting electrode is the ion trap mold mass spectroscopy of claim 6 characterized by being the curved octopole electrode.

[Claim 8] Said deflection and mass discontinuous-selection section are the ion trap mold mass spectroscopy of claim 1 characterized by having arranged each class at the serial so that it may have four parallel pin electrodes two or more sets and the inter-electrode medial axis of each class may cross.

[Claim 9] The ion trap mass-analysis approach of carrying out the ion beam included in said ion which has the deflection selection step which deflects the ion beam containing the sample ionized by quadrupole electric field in the ion trap mass-analysis approach of having the capture step which catches an ion beam, and the step which carry out the mass separation of the caught ion, and chooses the mass of ion, and was chosen at said deflection selection step after said deflection selection step being captured at said capture step as the description.

[Claim 10] It is the ion trap mass analysis approach of claim 9 which said deflection selection step has the step which impresses high-frequency voltage to four pin electrodes which are curving in the same direction based on the mass number pair charge ratio of the ion which should be chosen, and is characterized by said ion beam passing through between said four pin electrodes.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention supplies the solvent molecule and sample which were ionized to ion trap inter-electrode, and relates to the ion trap mold mass spectroscopy and ion trap analytical method which analyze the mass of ion to high sensitivity.

[0002]

[Description of the Prior Art] When carrying out mass analysis of the mixture sample, highly precise analysis is attained by combining the preprocessor which carries out segregation of the mixture sample, and a mass spectrograph. Usually, a gas chromatograph, a liquid chromatograph, etc. are used as preprocessor. In the case of a gas chromatograph, in the case of inert gas and a liquid chromatograph, in the gas chromatograph and liquid chromatograph of preprocessor, the difference in adsorption power of as opposed to a sink and a stationary phase for a mixture sample has separated the mixture sample with the solvent into the column in which the stationary phase was put. The sample by which segregation was carried out by preprocessors, such as a gas chromatograph and a liquid chromatograph, is ionized before flowing into an ion trap mold mass spectrograph. At this time, a solvent molecule is ionized simultaneously, and what is not ionized but exists in inside with a neutral condition is produced. Since the solvent molecule of a neutral condition causes a noise at the time of detection, it is necessary to remove it.

[0003] It indicates JP,5-325882,A and JP,7-85834,A deflecting the ion beam in which a solvent molecule and a sample are contained using a deflecting electrode, supplying it to the mass analysis section, and removing the neutral molecule which is not deflected.

[0004]

[Problem(s) to be Solved by the Invention] Although a neutral molecule and ion are separable using the deflecting electrode of the above-mentioned conventional technique, there is no mass selectivity of ion and the ionized solvent molecule cannot be removed.

[0005] Since the solvent molecule and sample which were ionized are caught by ion trap inter-electrode together in the case of the conventional ion trap mold mass spectrograph, the consistency of the ion of ion trap inter-electrode space becomes large too much, resolution may fall, or a mass shift may occur, and the analysis engine performance may fall. In order to maintain and carry out mass analysis of the analysis engine performance, a limitation is in the number of the ion which can be caught to ion trap inter-electrode, and mass analysis of a lot of samples cannot be carried out at a time. Since the about 3-5 figures of the numbers of sample ion of number [especially] of the solvent molecules ionized when using a liquid chromatograph as preprocessor increase, it occupies a majority of ion with which solvent ion was caught by ion trap inter-electrode, and the problem it becomes impossible to supply to mass analysis the sample ion trap inter-electrode of a complement produces it.

[0006] Although unnecessary solvent ion may be immediately detached by mass and you may remove from ion trap inter-electrode after supplying the solvent molecule and sample which were ionized to ion trap inter-electrode, the solvent ion of the large quantity destabilized in this case adhering to the stanchion of an electrode etc., distorting ion trap inter-electrode electric field, and reducing the analysis engine performance is also considered.

[0007] the concentration of the sample ion which should carry out mass analysis of the object of this invention -- raising -- a high resolution -- and it is a higher S/N ratio and is in offering the ion trap mold mass spectroscopy and ion trap mass spectrometry which can perform mass analysis.

[0008]

[Means for Solving the Problem] The ion beam in which the deflection and the mass discontinuous-selection section which deflects the ion beam containing the ionized sample, and chooses the mass of ion contain the ion with which the preceding paragraph of the ion trap mold mass analysis section was equipped, and which was chosen in a deflection and the mass discontinuous-selection section has the description of this invention of attaining the above-mentioned object in the ion trap mold mass analysis section being supplied. According to this description, even if a neutral molecule is supplied to a deflection and the mass discontinuous-selection section with the ionized sample, mass selection of the ion beam is deflected and made in a deflection and the mass discontinuous-selection section, but since a neutral molecule goes straight on in the direction which carried out incidence, the selected ion and the selected neutral molecule are separated. Only the ion beam containing the selected ion is supplied to the ion trap mold mass analysis section. low [by a lot of unnecessary ion], since the concentration of the sample ion by which mass analysis should be carried out in the ion trap mold mass analysis section can be raised -- resolution -- the ** which does not receive adverse effects, such as-izing and generating of the noise by the neutral molecule, -- more -- a high resolution -- and mass analysis can be performed by the higher S/N ratio.

[0009] Moreover, between pin electrodes, curved quadrupole electric field are formed along with the bow of a pin electrode by having four pin electrodes with which a deflection and the mass discontinuous-selection section are curving in the same direction. The ion beam supplied to a deflection and the mass discontinuous-selection section moves quadrupole electric field along with the bow of a pin electrode, and although mass selection is made, since a neutral molecule goes straight on in the direction which carried out incidence, it can separate the selected ion and the selected neutral molecule.

[0010] Moreover, high-frequency voltage is impressed to a pin electrode from an RF generator, and quadrupole electric field are formed between pin electrodes. When it is that in which high-frequency voltage does not have a dc component, the ion below the mass number pair charge ratio called for based on the amplitude and frequency of alternating voltage is removed from between pin electrodes. When high-frequency voltage has a dc component and an alternating current component, the ion of the range of a mass number pair charge ratio called for based on the magnitude of direct current voltage, the amplitude of alternating voltage, and a frequency is removed from between pin electrodes. When it has the alternating current component whose high-frequency voltage is two, the unnecessary ion with which the mass range of the ion which should be carried out mass analysis is dotted can be eliminated.

[0011] Moreover, an ion beam may be deflected with a deflecting electrode, a neutral particle can be removed, and ion may be chosen with four parallel pin electrodes. For example, if the octopole electrode which curved as a deflecting electrode is used, since the octopole electrode is excellent in the stability of ion transport, it can lessen ion loss by the deflection of an ion beam, and can perform mass analysis of high sensitivity more.

[0012] Moreover, if it arranges to a serial, using the group of four parallel pin electrodes two or more so that each inter-electrode medial axis may cross, an ion beam is deflected between each class, a neutral particle can be removed, ion is chosen by each class, or unnecessary ion is removed, and also when the mass range which should be chosen is discontinuous, unnecessary ion and an unnecessary neutral particle can be removed.

[0013]

[Embodiment of the Invention] (Example 1) The ion trap mold mass spectroscope which is the 1st example of this invention is explained. Drawing 1 is the schematic diagram of the ion trap mold mass spectroscope of this example. Before the ion trap mold mass spectroscope of this example performs mass analysis in the ion trap mold mass analysis section 5, they are a deflection and the mass selection section 10, and tends to obtain the analysis result of a high resolution and a high S/N ratio by raising the concentration of the sample ion which should remove and carry out mass analysis of unnecessary ion and an unnecessary neutral molecule.

[0014] The ion trap mold mass spectroscope of this example The mixture sample which is the object of mass analysis The gas chromatograph which carries out segregation (GC) and a liquid chromatograph Preprocessor 2, and the sample and solvents by which segregation was carried out, such as (LC) The focusing lens system 4 and the focusing lens system 4 which converge the ion beam supplied from the deflection and the mass selection section 10, and the deflection and the mass selection section 10 which remove unnecessary ion and an unnecessary neutral molecule from the ion beam in which the ionization

section 3 and the solvent molecule to ionize, and a sample are contained The mass separation of the sample ion contained in the ion beam which passed The ion trap mold mass analysis section 5 to perform, The ion detached by mass in the ion trap mold mass analysis section 5 It has RF generator 20 of the detector 6 to detect, the data-processing section 7 which processes the class and number of the detected ion, and ** a deflection and for mass selection section 10, the high-frequency-voltage power source 8 for ion trap mold mass analysis section 5, and the control section 9 that controls these actuation.

[0015] First, the ion trap mold mass analysis section 5 is explained. The ion trap mold mass analysis section 5 is shown in drawing 2 . The ion trap mold mass analysis section 5 is opposed so that the ring electrode 51 and it may be inserted, and it consists of two end cap electrodes 52 and 53. Direct current voltage U and high-frequency voltage Vcosomegat are impressed to each inter-electrode one from the high-frequency-voltage power source 8, and quadrupole electric field are built by inter-electrode space.

[0016] The ion beam which was detached by a deflection and mass in a deflection and the mass selection section 10, and passed the focusing lens system 4 passes along the main opening 13 of the end cap electrode 52, is supplied between the ring electrode 51 and the end cap electrodes 52 and 53, and is caught by quadrupole electric field.

[0017] The stability of the orbit of the ion caught by this quadrupole electric field becomes settled with a value and q value of (1) type. a value and q value are the ring electrode bore r0. It is given by the amplitude V of the direct current voltage U impressed to an electrode, and high-frequency voltage, the angular frequency omega of high-frequency voltage, and mass pair charge ratio m/Z of ion. here -- Z -- the valence of ion, and m -- mass and e -- base -- a charge is expressed.

[0018]

[Equation 1]

$$a = \frac{8 e U}{r_0^2 \Omega^2} \cdot \frac{Z}{m}, \quad q = \frac{4 e V}{r_0^2 \Omega^2} \cdot \frac{Z}{m} \quad \dots (1) \text{ 式}$$

[0019] Each ion supplied to ion trap inter-electrode has a value according to mass pair charge ratio m/Z (a, q), respectively.

[0020] The range of a and q to which ion has a stable orbit in drawing 3 in ion trap inter-electrode space (stable zone) is shown.

[0021] High-frequency voltage Vcosomegat When impressed by the ring electrode 51, since a value of each ion is set to 0 with direct current voltage U= 0, each ion will be located on q shaft which it is among [a= 0] stable zones. Each ion is q= 0 to q= 0.908 on q shaft to order, although the value of mass pair charge ratio m/Z is small from a large thing. It is located in the range of until. All the ion located on q shaft of a stable zone vibrates to stability in inter-electrode space, and is caught by inter-electrode. Then, the ion detached by mass is detected by the detector 6 through the main opening 55 of the end cap electrode 53, and a mass spectrum is obtained as a final analysis result.

[0022] Next, a deflection and the mass selection section 10 are explained.

[0023] The deflection quadrupole electrode system 11 of a deflection and the mass selection section 10 is shown in drawing 4 . The deflection quadrupole electrode system 11 has four pin electrodes 12a, 12b, 12c, and 12d, and it is carrying out the comparable bow of each pin electrode 12 in the same direction so that uniformly [each inter-electrode distance]. Four pin electrodes 12 are curving to serpentine [loose] so that the direction as for which the ion to the deflection quadrupole electrode system 11 carries out incidence, and the direction ion carries out [a direction] outgoing radiation from the deflection quadrupole electrode system 11 may become almost parallel. The superposition electrical potential difference (** (Uq+Vqcosomegaqt)) of the direct current voltage Uq and high-frequency voltage Vqcosomegaqt from which a sign differs with an adjacent pin electrode is impressed to four pin electrodes 12.

[0024] The electrical potential difference impressed to a pin electrode 12 is controlled by the control section 9. High-frequency-voltage**Vqcosomegaqt impressed to four pin electrodes 12 at this time A frequency is the high-frequency voltage Vcosomegat impressed to the ring electrode 51 of the ion trap mold mass analysis section 5. You may differ on a frequency and a theoretical target. however, the frequency of the high-frequency voltage impressed to the ring electrode 51 of the ion trap mold mass analysis section 5 and the frequency of the high-frequency voltage impressed to four pin electrodes 12 -- the same -- or if it sets up an integral multiple, 1 time for an integer, etc., since it branches and the

electrical potential difference impressed to the ring electrode 51 can be impressed also to the deflection quadrupole electrode system 11, duplication of a high-frequency-voltage power source is avoidable.

[0025] Four pin electrodes 15 of the deflection quadrupole electrode system 11 explain below the principle which can remove unnecessary ion and an unnecessary neutral molecule.

[0026] First, the fundamental quadrupole electric field made among four parallel pin electrodes 14 of the quadrupole electrode system 13 as shown in drawing 5 explain that mass selection of ion can be performed. Only the point which is not curving only differs from four pin electrodes 12 of the deflection quadrupole electrode system 11, and an inter-electrode distance and the inter-electrode electrical potential difference impressed of four pin electrodes 14a, 14b, 14c, and 14d are the same. If an electrical potential difference is impressed to four pin electrodes 14, quadrupole electric field will be built between pin electrodes 14.

[0027] It becomes settled whether ion penetrates the inside of this quadrupole electric field to stability with a value and q value which are given by (2) formulas. a value and q value are the mesial magnitude rq of two inter-electrode distance which is on the diagonal line with the square which four pin electrodes 14 make. It is given by the amplitude V_q of the direct current voltage U_q impressed to a pin electrode 14, and high-frequency voltage, angular-frequency ω_q , and also mass pair charge ratio m/Z of ion. here $-\ Z -$ the valence of ion, and $m -$ mass and $e -$ base $-$ a charge is expressed.

[0028]

[Equation 2]

$$a_q = \frac{8 e U_q}{r_q^2 \Omega_q^2} \circ \frac{Z}{m}, \quad q_q = \frac{4 e V_q}{r_q^2 \Omega_q^2} \circ \frac{Z}{m} \quad \dots (2) \text{ 式}$$

[0029] Each ion supplied between pin electrodes 15 has a value according to mass pair charge ratio m/Z (a_q , q_q), respectively.

[0030] a_q in case ion penetrates between pin electrodes 14 to stability at drawing 6, and the range of q_q (stable transparency field) are shown. Although each ion is located in the a_q - q_q flat surface of drawing 6 with the value of (a_q , q_q) and the ion of a stable transparency field penetrates between pin electrodes 14 to stability, an orbit destabilizes the ion besides a stable zone and it cannot penetrate between pin electrodes 14.

[0031] If only high-frequency-voltage** $V_q \cos \omega_q t$ is impressed to a quadrupole electrode, it is a_q of each ion at $U_q=0$. Since a value is set to 0, each ion will be located on q_q shaft which is $a_q=0$ among stable zones. From what has the large value of mass pair charge ratio m/Z , although each ion is small, it is located on q shaft at order in the direction where $q=0$ to q becomes large. Since it is the range from $q=0$ to $q_q=0.908$, the stable zone on q shaft is q_q beyond $q_q=0.908$. All ion with a value, i.e., the ion with mass number pair charge ratio m/Z below the mass number pair charge ratio equivalent to $q_q=0.908$, cannot penetrate between pin electrodes 14.

[0032] Therefore, q_q of unnecessary ion Electrical-potential-difference** $V_q \cos \omega_q t$ impressed to a pin electrode 14 so that a value may come outside a stable transparency field By adjusting, unnecessary ion is removable. Thus, between pin electrodes can be made to penetrate selectively according to mass pair charge ratio m/Z of ion by adjusting electrical-potential-difference** $V_q \cos \omega_q t$ impressed to the pin electrode 14 of the quadrupole electrode system 13.

[0033] Electrical-potential-difference** $V_q \cos \omega_q t$ impressed to the pin electrode 12 shown in drawing 4 also by this example Mass selection of the ion same with having adjusted and mentioned above can be performed. Moreover, the quadrupole electric field made between the pin electrodes 12 of the deflection quadrupole electrode system 11 are curving along with the curved pin electrode 12. Although the selected ion is deflected by curved quadrupole electric field, and meets and moves between pin electrodes 12 and outgoing radiation is carried out from the deflection quadrupole electrode system 11, since a neutral molecule goes straight on in the direction which carried out incidence, it is separated with the selected ion. Therefore, a neutral molecule is removed and only the selected ion is conveyed to the ion trap mold mass analysis section 5.

[0034] To drawing 7, solvent molecules are 90amu(s). Below, it is 90amu. The example of the orbital analysis of the ion in the deflection quadrupole electrode system 11 at the time of using the ion of the following mass numbers as unnecessary ion is shown. High-frequency-voltage** $V_q \cos \omega_q t$ was set up so that it might be equivalent to (0, 0.908) of drawing 8 in (a_q , q_q) of the unnecessary ion of 90amu(s).

[0035] According to the analysis result of drawing 7, it is 90amu. Although it becomes unstable [the following unnecessary ion] and is removed from the deflection quadrupole electrode system 11, to high mass number ion, it has passed from it to stability. Moreover, it has turned at the medial axis of the ion trajectory which passed to stability in accordance with the configuration of the curved pin electrode 12, and the ion passed to stability can advance to the ion trap mold mass analysis section 5. However, since a neutral molecule goes straight on, without deviating by quadrupole electric field, it cannot advance to the ion trap mass analysis section 5.

[0036] therefore, low [by a lot of unnecessary ion], since according to the ion trap mold mass spectroscopy of this example unnecessary ion and an unnecessary neutral molecule can be removed and the concentration of the sample ion which should be carried out mass analysis can be raised by the deflection quadrupole electrode system 11 -- resolution -- the ** which does not receive adverse effects, such as--izing and generating of the noise by the neutral molecule, -- more -- a high resolution -- and mass analysis can be performed by the higher S/N ratio.

[0037] moreover, by the deflection quadrupole electrode system 11 explained by this example Before and after an ion beam passes the deflection quadrupole electrode system 11, since the beam travelling direction is almost parallel As shown in drawing 9, it can respond easily only by shifting a shaft and installing a deflection and the mass selection section 10 of this example also to the existing equipment the direction as for which ion carries out incidence from the ion source, and whose shaft of the ion trap mold mass analysis section 5 and the gap electrodes 52 and 53 correspond.

[0038] (Example 2) Next, the 2nd example of this invention is explained. In this example, in the deflection quadrupole electrode system 11 of a deflection and the mass selection section 10, as shown in drawing 10, the pin electrode 15 incurvated so that the direction of incidence and the direction of outgoing radiation of an ion beam might differ from each other was used. However, the pin electrode 15 has incurvated the pin electrode 12 so that inter-electrode distance may not change, and so that the direction of incidence and the direction of outgoing radiation of an ion beam may make about 90 degrees. Thus, if the pin electrode 12 is incurvated, it is separable with the selected ion also to the neutral molecule which carries out incidence to the deflection quadrupole electrode system 11 with various include angles.

[0039] according to this example -- a neutral molecule -- more -- being removable -- more -- a high resolution -- and mass analysis can be performed by the higher S/N ratio.

[0040] (Example 3) The 3rd example of this invention is explained. In this example, as shown in drawing 11, not only the high-frequency voltage $Vq\cos\omega qt$ but the direct current voltage Uq ($Uq \neq 0$) impresses the electrical potential difference impressed to the pin electrode 12 of the deflection quadrupole electrode system 11. (2) By the formula, the point (aq, qq) of ion is located in a line on the straight line of $aq=2 Uqqq/Vq$ of drawing 12. This $aq=2 Uqqq/Vq$ Only the ion which corresponds in the field where a stable transparency field laps with a straight line passes through the inside of a quadrupole electrode to stability, an orbit destabilizes the other ion kind and it is removed. If the mass range of the ion which passed through the inside of a quadrupole electrode to stability is set to $M1$ [amu] - Mn [amu], the mass spectrum eventually obtained in the ion trap mold mass analysis section 5 will be restricted within the limits of $M1$ [amu] - Mn [amu], as shown in drawing 13.

[0041] therefore, the case where the mass range of the ion which should be carried out mass analysis is known -- a upper limit and a lower limit -- corresponding (aq, qq) -- what is necessary is just to adjust electrical-potential-difference ** ($Uq+Vq\cos\omega qt$) impressed to a pin electrode 12, as it is in a stable zone

[0042] Moreover, as shown in drawing 14, $Uq+Vq\cos\omega qt$ is adjusted so that the straight line of $aq=2 Uqqq/Vq$ may cross near the top-most vertices of a stable transparency field. Thus, mass pair charge ratio value $M0$ which corresponds near the top-most vertices of a stable transparency field by drawing 14 when an electrical potential difference is impressed to a pin electrode 12 The ion which it has carries out the stable transparency of the quadrupole inter-electrode, and all the other ion is removed. Moreover, a neutral molecule is removed from the deflection quadrupole electrode system 11 like the 1st example. Therefore, mass pair charge ratio value $M0$ Incidence only of the ion which it has will be carried out into the ion trap mold mass analysis section 4, and a trap will be carried out to ion trap inter-electrode, and it will carry out stable oscillation.

[0043] since the selection range of ion can be limited [according to this example] more in addition to

the effectiveness by the 1st example -- more -- a high resolution -- and mass analysis can be performed by the higher S/N ratio.

[0044] (Example 4) Next, the ion trap mold mass spectroscope which is the 4th example of this invention is explained. The schematic diagram of the ion trap mold mass spectroscope of this example is shown in drawing 15. The ion trap mold mass spectroscope of this example establishes the auxiliary alternating-voltage power source 21 for deflection quadrupole electrode system 11, and differs from the ion trap mold mass spectroscope (drawing 1) of the 1st example in the place which impresses $V_{qcos\omega t} + v_{q'}cos\omega t$ to the pin electrode 15 of the deflection quadrupole electrode system 11. The auxiliary alternating-voltage power source 21 is controlled by the control section 9.

[0045] A natural-frequency frequency changes with values of the mass pair charge ratio of ion within a quadrupole electrode as well as the inside of an ion trap electrode. Therefore, as shown in drawing 16, it is auxiliary alternating-voltage $v_{q'}cos\omega t$ to a pin electrode 12. By impressing and generating auxiliary alternating current electric field between pin electrodes 12, specific ion can be made into a resonance state and it can remove from between pin electrodes 12. For example, it is auxiliary alternating-voltage $v_{q'}cos\omega t$ so that only this unnecessary ion ($M=Ms$) may resonate, when mass within the limits of the ion which should be carried out mass analysis is dotted with unnecessary ion ($M=Ms$), as shown in drawing 17. If it adjusts, this unnecessary ion can be eliminated.

[0046] (Example 5) Next, the 5th example of this invention is explained. In this example, the quadrupole electrode system 13 shown in a deflection and the mass selection section 10 at drawing 18, and the decelerating electrode 31 installed in incidence opening of the quadrupole electrode system 13 and the convergent-lens system 32 are used. The quadrupole electrode system 13 has four parallel pin electrodes 14 explained by drawing 5 of the 1st example.

[0047] If incidence of the ion is carried out so that the medial axis of a pin electrode 15 may be intersected, a decelerating electrode 31 and the convergent-lens system 32 will slow down and converge an ion beam. The ion beam which it slowed down and converged enters between pin electrodes 14, and the selected ion passes the quadrupole electrode system 13. Since a neutral particle goes straight on, without being influenced of a decelerating electrode 31 and the convergent-lens system 32, it is removed from the quadrupole electrode system 13.

[0048] According to this example, four pin electrodes 14, a decelerating electrode 31, and the convergent-lens system 32 are installed, and since the mass of ion can be chosen only by carrying out incidence of the ion beam so that the shaft of the quadrupole electrode system 13 may be intersected, a deflection and the mass selection section 10 can be manufactured easily.

[0049] (Example 6) Next, the 6th example of this invention is explained. In this example, as shown in a deflection and the mass selection section 10 at drawing 19, the deflecting electrode 33 installed by incidence opening of the quadrupole electrode system 13 and the quadrupole electrode system 13 and the convergent-lens system 32 are used. The quadrupole electrode system 13 has four parallel pin electrodes 14.

[0050] If incidence of the ion is carried out to a deflecting electrode 33, an ion beam will be deflected by the deflection electric field which a deflecting electrode 33 builds, and it will converge by the convergent-lens system 32 by it. The deflected ion beam enters between pin electrodes 15, and the selected ion passes the quadrupole electrode system 13. Since a neutral particle goes straight on, without being influenced of the deflection electric field which a deflecting electrode 33 builds, it is removed from the quadrupole electrode system 13. Moreover, as shown in drawing 20, a deflecting electrode 33 and the convergent-lens system 32 may be installed in outgoing radiation opening of the quadrupole electrode system 13. Mass selection of the ion which carried out incidence between the pin electrodes 14 of the quadrupole electrode system 13 is made between pin electrodes 14, and a neutral molecule is removed by the deflecting electrode 33 after that.

[0051] According to this example, since four parallel pin electrodes 14, a deflecting electrode 33, and the convergent-lens system 32 can be used, a deflection and the mass selection section 10 can be manufactured easily.

[0052] (Example 7) Next, the 7th example of this invention is explained. In this example, multipole electrodes, such as the quadrupole electrode system 13 and the deflection octpole electrode system 34, are used for a deflection and the mass selection section 10. In this example, the mass of an ion beam is chosen by the quadrupole electrode system 13 in which mass selectivity is excellent, the deflection octpole electrode system 34 is incurvated as shown in drawing 21, and an ion beam is deflected. Since

the deflection octopole electrode system 34 is excellent in the stability of ion transport, ion follows the bow of an electrode etc. and it is deflected to stability. Moreover, as shown in drawing 22, reverse is sufficient as the sequence of mass selection by the quadrupole electrode system 13, and the beam deflection in the deflection octopole electrode system 34.

[0053] According to this example, by making mass selection of the ion beam by the quadrupole electrode system 13, and making stability deflect an ion beam by the deflection octopole electrode system 34, ion loss by the deflection of an ion beam is lessened, and mass analysis of high sensitivity can be performed more.

[0054] (Example 8) Next, the 8th example of this invention is explained. In this example, as shown in drawing 23, two or more quadrupole electrode systems 13 which change from four parallel pin electrodes 14 to a deflection and the mass selection section 10 are used. The 4-fold each pole electrode system 13 is installed so that each medial axis may cross. Mass selection is made by the 4-fold each pole electrode system 13, and an ion beam is deflected between the adjacent quadrupole electrode systems 13. A neutral molecule is removed between the adjacent quadrupole electrode systems 13.

[0055] Moreover, unnecessary ion which is different by the 4-fold each pole electrode system 13 can also be removed, and the ion of the range of the mass pair charge ratio limited more can be chosen. When the ion whose mass pair charge ratio M is less than $[M1]$, the ion which is $M2 (M1 < M2)$, and the ion which is $M3 (M1 < M3)$ are contained as unnecessary ion in the sample, for example, by quadrupole electrode system 25—a $M1$ Remove the ion of the following mass pair charge ratios, and auxiliary alternating voltage is impressed to quadrupole electrode system 25—b. $M=M2$ The ion of a mass pair charge ratio is removed, and auxiliary alternating voltage is impressed to quadrupole electrode system 25—c, and it is $M=M3$. What is necessary is just to remove the ion of a mass pair charge ratio (refer to drawing 24). In order to remove unnecessary ion which is different by the 4-fold each pole electrode system 13, the auxiliary alternating voltage impressed to a pin electrode 14 by the 4-fold each pole electrode system 13 is adjusted, respectively.

[0056] since unnecessary ion and an unnecessary neutral particle can be removed also when the mass range which should be chosen is discontinuous according to this example — more — a high resolution — and mass analysis can be performed by the higher S/N ratio.

[Effect of the invention] According to this invention, even if a neutral molecule is supplied to a deflection and the mass discontinuous—selection section with the ionized sample, mass selection of the ion beam is deflected and made in a deflection and the mass discontinuous—selection section, but since a neutral molecule goes straight on in the direction which carried out incidence and it can raise the concentration of the sample ion by which the selected ion and the selected neutral molecule should be separated and mass analysis should be carried out in the ion trap mold mass analysis section low [by a lot of unnecessary ion] — resolution — the ** which does not receive adverse effects, such as—izing and generating of the noise by the neutral molecule, — more — a high resolution — and mass analysis can be performed by the higher S/N ratio.

[0058] Moreover, a deflection and the mass discontinuous—selection section can separate the selected ion and the selected neutral molecule by having four pin electrodes which are curving in the same direction.

[0059] Moreover, high—frequency voltage is impressed to a pin electrode from an RF generator, and quadrupole electric field are formed between pin electrodes. When it is that in which high—frequency voltage does not have a dc component, the ion below the mass number pair charge ratio called for based on ** and the frequency of alternating voltage is removed from between pin electrodes. When high—frequency voltage has a dc component and an alternating current component, the ion of the range of a mass number pair charge ratio called for based on ** and the frequency of the magnitude of direct current voltage and alternating voltage is removed from between pin electrodes. When it has the alternating current component whose high—frequency voltage is two, the unnecessary ion with which the mass range of the ion which should be carried out mass analysis is dotted can be eliminated.

[0060] Moreover, an ion beam may be deflected with a deflecting electrode, a neutral particle can be removed, and ion may be chosen with four parallel pin electrodes. If the octopole electrode which curved to the deflecting electrode is used, ion loss by the deflection of an ion beam can be lessened, and mass analysis of high sensitivity can be performed more.

[0061] Moreover, if it arranges to a serial, using the group of four parallel pin electrodes two or more so

that each inter-electrode medial axis may cross, also when the mass range which should be chosen is discontinuous, unnecessary ion and an unnecessary neutral particle can be removed.

[Translation done.]